1.1 General introduction

The oceans covering approximately 70% of the earth crust contain four major sub systems namely; the seawater, suspended particulate material, sediment and the biota. All the naturally occurring elements are considered to be present in ocean in almost all possible chemical forms in varying concentrations. Input of elements is either as dissolved form or as particulate or suspended form. Sediment, which acts as the sink and reservoir, plays the key role in removal. The biogeochemical processes such as acid-base reactions, oxidation–reduction, complexation, adsorption at interfaces, precipitation and dissolution of solid and distribution of solutes between aqueous and non-aqueous phases regulate the bioavailability of the element in the system. The suspended materials on sinking are subjected to changes in composition through processes such as aggregation, disaggregation, scavenging, decomposition and dissolution (Chester, 1990). In surface waters of coastal and estuarine regions, suspended materials are high and variable than in open ocean. Nearshore sediments are strongly
influenced by the land masses, while deep sea sediments are influenced by the reactivity between particulate and dissolved components in the water column. The surface runoff delivers elements into the coastal zone, which get progressively diluted in the open ocean. However, the coastal zone is not simply a reservoir of these materials, as they are distributed among water, sediment and living organisms, providing an environment of intense biogeochemical reactions (Figure 1.1). The dominance of one or many of these processes decides the fate of elements and results in their retention in the region or export to the ocean.

Figure 1.1. Schematic representation on the processes influencing the fate and pathways of elements in the coastal margins (from Simpson, 1994).

The sources of the dissolved and particulate elements in rivers include rock weathering, atmospheric deposition, decomposition of organic matter and anthropogenic activities. The inputs are generally based on the basin
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properties of drainage area such as lithology, relief, land use pattern, vegetation etc. The materials undergo various physio-chemical changes in the estuary before ultimately reaching the ocean. Fluxes from large rivers are used to estimate coastal inputs (Dupre et al., 1996) and erosional process on a global scale (Stallard and Elmound, 1987). Most of the studies have focused on the dissolved and particulate phases of the river-estuarine systems. Chemical changes are however, noted in the sediments of small rivers (drainage basin <10,000 km²), which from numerous numbers may actually contribute much more elemental fluxes (Milliman and Syvitski, 1992; Albarede and Semhi, 1995).

The conventional paradigm for the behavior of reactive materials in coastal marine ecosystems has been to identify the processes by which dissolved and particulate materials are associated with minerals settling to sediments. Because of the dynamic nature of these systems, estuarine processes are complex and their transformations often remain obscure. Turbulent mixing of freshwater and seawater can generate rapid changes in Eh, pH, salinity, and trace element concentrations (Feely et al., 1981). Superimposed on this variability are the biological processes acting on time scales of seconds to days (Hedges and Keil, 1999). Hence, it is difficult to understand the origins, pathways, and fates of dissolved and particulate materials in coastal marine systems, and especially in estuaries.

Increase human interventions in estuaries and coastal zones over the last few decades can disrupt the natural equilibrium and the biotic composition of the respective ecosystems. The main causes for such changes are introduction of untreated and partially treated (industrial and urban) sewage rich in organic substances and plant nutrients, seepage from agricultural/aquaculture fields and animal husbandry. Sediments represent
one of the ultimate sink for heavy metals discharged into the aquatic environment. These metals occur in sediments, adsorbed as ions, hydroxides, oxides, phosphates, silicates, carbonates, sulphates, sulphides and organometalic compounds (Jenne, 1976). These metals are not necessarily fixed permanently by the sediments and may be released to the water column under favorable conditions. Thus in aquatic system, sediments may be both a carrier and a source of metals. However, factors such as pH, redox potential and salinity play an important role in the mobilization of particulate metals (Kersten and Förstner, 1987).

The role of rivers and estuaries in transporting detrital materials from continents to oceans is paramount, being 10 times that of glaciers and 100 times that of wind (Goldberg, 1976). They carry metals in solution, adsorbed on inorganic solids as cations, on organic solids and in detrital crystalline materials (Gibbs, 1973). The human impact on the geochemical cycling of metals is predominantly a localized one, involving the redistribution of the element from the earth's crust. Though they undergo some perturbation during these processes, some metals are rapidly returned to the lithosphere by sedimentary deposition. As they are persistent and non-biodegradable, they cannot be eliminated but can only be relocated or converted into forms of reduced accessibility or bioavailability (Barbour and Taylor, 1988). Hence, estimation of metals in marine sediments is an important tool for distinguishing between the various carrier phases and to delineate the processes that lead to their enrichment in the sediments. Of special interest is the study of those metals, which have an affinity for biota, such as Cu, Zn, Co, Cr, Ni as well as Fe that have a nutrient-like distribution in the oceans. The enrichment of these metals in marine sediments has been related to the high productivity zone in the hemi-pelagic and pelagic
environments, where organic matter in the water column plays an important role in their transport from seawater to the bottom sediments (Collier and Edmond, 1984; Martin and Thomas, 1994). Some metals are accumulated in marine sediments by precipitation from seawater as hydroxides, as is the case of Fe-Mn (Landing and Bruland, 1987) and elements scavenged by them by their incorporation and/or adsorption to authigenic mineral phases (Altschuler, 1980). Sediments are major repositories for metals and, in addition to providing the environmental status; they are also used to estimate the level of pollution in a region (Burton and Scott, 1992; Caccia et al., 2003).

The west coast of India is environmentally more sensitive than the east coast primarily because it is bordering one of the most sensitive ecosystems in the world, the Arabian Sea. The environmental property of the northern Arabian Sea is unique which manifests in rich biological production throughout the year through different processes and thus, explain for the Arabian Sea ‘Paradox’ (Mathupratap et al., 1996). The mid-depth oxygen deficiency in the Arabian Sea is perhaps the most severely observed anywhere in oceans, as the concentration within \( \sim 150 - 1000 \) m are less than 0.1 ml/l within a large part of central and northeastern Arabian Sea (Naqvi and Jayakumar, 2000). This zone is characterised by intense denitrification, which is observed only in 3 regions among world oceans, the other two being observed in the Pacific. With such a delicate biogeochemical balance that exists in the oceanic oxygen-deficient zones, the Arabian Sea will perhaps be among the first to react to potential anthropogenic perturbations such as increased nutrient/organic loading (Naqvi et al., 2000). Any alterations in the rate of mid-depth water renewal or in subsurface oxygen demand may bring about large changes in chemical fluxes. Similarly, an expansion of the oxygen minimum zone, particularly
towards the coastal zone, may also have deleterious effects on biological resources as evident from mass mortality of fish reported off Cochin during southwest monsoon, 1998 (Naqvi et al., 1998). It is still not clear as to how the suboxic ecosystem in the Arabian Sea will respond to changes induced by man.

There is an apprehension that environmental deterioration of coastal and estuarine waters will inevitably have consequences for the Arabia Sea’s ecosystem. The symptoms are there to show considerable impact of deterioration of estuarine waters on the coastal as well as shelf ecosystem (Nair et al., 1991; Naqvi et al., 2000; Jayakumar et al., 2001). The emerging industrial establishments and human settlements along the west coast of India, thus necessitates a critical evaluation of the nature and quantum of inputs to the Arabian Sea as well as their regional assimilative capacities. If there is a possible threat to the well being of the living resources of EEZ of India, then the southeastern Arabian Sea is one of the prime locations affecting the most.

As estuaries are geochemical barriers regulating the export of materials, emerging metropolises like Cochin necessitates information on the fate of metals in the coastal environment. The booming city of Cochin has population of nearly 1.5 million (Anon, 1998) and 60% of the chemical industries of Kerala are situated in this area. Cochin estuarine system is the largest of its kind on the west coast of India with an area of 256 Km². Cochin estuarine system comprises one of the most important harbour and industrial centers in the west coast of India. It was reportedly unpolluted, sustaining a rich shell and fin fishery and variety of other organisms (Sankaranarayanan and Qasim, 1969). The anthropogenic influence in the estuary began in the second part of 19th century and continues to compound
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(Gopalan et al., 1983; Balachandran, 2002). The resident population (3 Million in 2002, @ > 4000 person.km$^{-2}$) and associated industrial activities result in a release of 0.104 Mm$^3$d$^{-1}$ of industrial wastes and 260 t.d$^{-1}$ of domestic sewage without proper treatment, polluting the lower estuary with nutrients, trace metals, organic matter and pesticides (CPCB, 1996; Sujatha et al., 1999; Menon et al., 2000; Balachandran et al., 2005). Even though numerous researchers have reported the trace metal distribution in the Cochin estuary (Venugopal et al., 1982; Nair et al., 1990; Nair, 1992; Padmalal et al., 1996; Balachandran et al., 2005; Balachandran et al., 2006) as well as in the coastal region (Murthy et al., 1973; Rajamaniamma, 1994; Laluraj and Nair, 2006), an integrated geochemical study involving trans-boundary exchange of the potentially toxic elements has not been carried out so far. The industrial typology includes fertilizer, pesticide, radio-active mineral processing, chemical and allied industries, petroleum refining and heavy metal process and fish processing. The fertilizer consumption in Kuttanad region (the main agricultural field draining to Cochin estuary) alone is reported to be 20,239 t y$^{-1}$ (Anon, 1998). The estuary receives organic wastes (~ 260t d$^{-1}$, Anon, 1998) and an annual dredge spoil from the harbor area to the tune of 107 m$^3$. A recent study on this coastal environment has brought out the different pathways of metal associations in coastal sediments on an annual scale (Balachandran et al., 2003; Balachandran et al., 2006). They observed that succession of southwest monsoon by winter and inter monsoon periods brought a distinct transformation in the behavior of metals from a rapid deposition to an organic association followed by sedimentary modifications to normalize the geochemical distribution. To summarize all, as the system has been subjected to irrational economic exploitation during the past five decades,
the environmental deterioration has ultimately resulted in ecological degradation.

1.2 Metals in aquatic system

In aquatic system, metals are present as dissolved ions, colloids, suspended and solid forms (sediments). The metal concentration strongly depends on the redox condition, pH, ionic strengths and scavenging activity. The ecological impact of metals largely depends on their form in water, capacity for complexation, sedimentation and bioaccumulation. Some trace metals are adsorbed on surface of suspended material or may be incorporated into the lattice of mineral such as iron and manganese oxides or in organic matter (Rognerud et al., 2000). Wayne and Markovics (1997) stated that the trace metals in sediment depend on the rock and on the weathering processes. Tang (1987) pointed out that the composition of a parent rock is the major factor affecting the trace metal content. The variability of metals in fine sediments is controlled more by hydraulic than geochemical activity by which, the sediments are transported and deposited (Marcus, 1996). The transition metals are present in sediment as insoluble hydroxides, carbonates and sulphides. Fe(OH)₃ and MnO₂ also influence the heavy metal deposition and distribution in sediments (Janne, 1976). Hence, metals in suspended and bed sediments are more sensitive than the metals in dissolved form and their level of contamination in an aquatic system (Turner and Millward, 2002).

In anoxic condition, metals and minor elements can vary as a function of prevailing redox potential (Calvert and Perdersom, 1993). Elements such as Cu, Cr, Co, Zn, Ni, V and Mo, which are soluble in oxic condition, are reduced to insoluble specious of lower valency under anoxic conditions. Hence, behavior of Cu, Cr, Co, Zn, Ni, V and Mo can be used as indicator
of sedimentation under different environmental conditions (Calvert and Perderson, 1993).

Metals are introduced into the ocean by river run off, winds, hydrothermal venting and anthropogenic activities. Rivers are a major source of particulate and dissolved metals, both of which are mobilised during the weathering of granitic and basaltic crust (Jérôme et al., 2008). Some of the cations are adsorbed onto the surface of clay minerals. Metals undergo different chemical reactions during estuarine mixing, which play an important role in establishing the oceanic composition of elements and act as a link between continent and oceans (Sholkovitz, 1993). The increase in ionic strength and pH in the estuary precipitates the resolubilised metals as oxyhydroxides and organomettalic colloids (Feely et al., 1981; Balachandran et al., 2005). The dissolved metals reaching the ocean tend to be more reactive than major ions and get deposited in sediments. Some of the metals are deposited as a component of wind-borne dust particles. In fact, atmospheric fall out is one of the largest oceanic inputs of some metals like, lead (Nel, 2005). Once metals are introduced into aquatic systems, the sinking particles carry them to sediments, where chemical reactions re-dissolve a significant fraction and diffuse across the sediment-water interface. Organic rich sediments are major sources of remobilized metals due to their affinity to organic matter (Derek and Elizabeth, 1986; Liang et al., 2008). In addition, the hydrothermal fluids associated with tectonic centers are enriched in trace metals as sulfides (Katja et al., 2007). Metals are also introduced by human activities via rivers and atmospheric transport. The alternate pathways include direct dumping of industrial and municipal wastes. The metal present in seawater undergoes rapid and efficient removal by adsorption, precipitation and incorporation into biogenic particles (Turner et al., 2008). These particles
enriched in metals eventually sink into the bottom, the process being termed as scavenging. The organic rich coastal and shelf sediments are susceptible to suboxic as well as oxic diagenesis. The suboxic condition leads to the enrichment of redox elements such as V, Cr, Co, Ni, Cu, Mo, Pb, U and Ce, whereas oxic sediment remove Mn and Fe under changing redox conditions (Jennifer and Steven, 1999; Shumei et al., 2008). The anoxic coastal sediments release metals diagenetically, while a fraction of these can escape back into the overlying waters.

Estuarine and oceanographic processes play an important role in linking the composition of sediments from rivers to oceans. Hence, geochemical composition of sediments provides global metal inputs to ocean. Some of the metals are removed during estuarine mixing (Martin et al., 1976; Sholkovitz and Elderfield, 1988; Elderfield et al., 1988). Sediment metal enrichment has been reported along the southwest coast of India (Nath et al., 2000). Metals introduced by domestic, industrial and mining activities are incorporated into sediments. Metals get accumulated in the estuarine and continental shelf sediments. The rare-earth elements (REEs) can be used to understand the geochemical evolution of earth's crust. REEs mobilize during weathering and undergo modifications (non-conservative) in the estuary (Sholkovitz et al., 1994). River sediments generally have a residual fraction and a liable fraction. REEs are sensitive to environmental changes such as redox condition, salinity, chelates, pH adsorption-desorption, complexation, precipitation etc. The metals can be divided into nutrient type and scavenging type according to their absorption capabilities (Chester, 1990). Nutrient-type metals behave similar to nutrients (NO₃, PO₄, and Si), suggesting their regulation through biological process. Scavenging-type elements are reactive and their distribution is determined by their adsorption
(hydrolytical and or/ oxidative) or removal onto particulate matter. For the present study, three groups of metals considered are non-transition, transition and rare earth elements, thorium and uranium.

1.2.1 Non-transition elements

The elements representing S and P block are included in the non-transition group. The metal reactivity depends on the ease with which electrons can be removed or their affinity towards electrons. The reactivity of elements in the periodic table decreases from left to right across a period and increases from top to bottom in a group. The group I elements are very reactive, soft, light and easily fusible. These alkali metals lose an electron readily and hence, are very reactive in water. The present study considers Rb and Cs from alkali metals. The alkaline earth (II group) elements possess a property intermediate between alkalis and rare earths metals. They lose two valence electrons to form ions with two plus charge. Beryllium is the least metallic element in the group and tends form covalent bonds in compounds. Alkaline earth metals are less active than the alkali metals. They react readily with halogens to form ionic salts, but react slowly with water. The present study includes Al and Ga from XIII group, representing P block. Aluminum is the third most abundant element in the earth's crust (7.4 %). Its oxide is stable and prevents corrosion, whereas Ga does not have this property. Bauxite (ore of aluminium) contain small amount of gallium. The two metals (tin and lead) in the XIV group of the periodic table are fairly unreactive and form ions with a $^+2$ or $^+4$. The non-transition elements are generally classified into conservative metals (Rb, Cs and Sr), nutrient and scavenging metals (Be, Ga and Ba), reactive and scavenging metals (Al and Pb) and anthropogenic and redox sensitive metals (Pb).
1.2.2 Transition elements

Transition elements (TEs) comprise of a series that share similar electronic configuration \([n^2 (n-1) d^{10}]\) and hence, similar chemical properties. The transition elements are commonly defined as the 30 elements with atomic numbers 21 to 30, 39 to 48, and 71 to 80. They are called transition elements because they are placed between the most reactive metals on the left and non-metals on the right. They resemble each other in several physical and chemical properties. As with all metals, the transition elements are both ductile and malleable, and conduct electricity and heat. The interesting thing about transition metals is that their valence electrons, or the electrons they use to combine with other elements, are present in more than one shell. This is the reason why they often exhibit several common oxidation states and showing redox nature under oxygen minimum condition / anoxic. The redox process may strongly affect the distribution of metals. The most distinctive manifestation of redox processes are encountered in suboxic and anoxic waters. In such waters, consumption of oxygen during the remineralisation of organic matter exceeds supply, so that \(\text{NO}_3, \text{Fe/Mn-oxyhydroxides}\) and finally \(\text{SO}_4\) are microbiologically reduced to continue this process. Suboxic waters contain neither dissolved oxygen nor dissolved sulphide and are poised by the intermediate electron acceptors (\(\text{NO}_3, \text{Fe/Mn-oxyhydroxides}\)). Anoxic waters are more strongly reducing and sulphide is present. Under these conditions, many metals change their oxidation state, which is mostly accompanied by dramatic change in solubility of metals such as \(\text{V, Cr, Mn, Fe, Co, Ni, Zn}\) and \(\text{Mo}\). For the present study, 15 transition elements were selected on the basis of abundance in nature, toxic effects and environmental interactions.
Rare earth elements (REEs), thorium and uranium

The REEs comprise 15 lanthanide elements (atomic numbers 57 to 71) as well as yttrium (at. no. 39). Because of the unique chemical properties, REEs are very useful in geochemical studies of earth and planetary systems (Goldberg et al., 1963; Taylor and McLennan, 1985; Bwire et al., 2003). They are extremely coherent in chemical behavior and have been subjected to intense investigation in marine geochemistry. All rare-earth elements occur in trivalent state with exception of Ce$^{4+}$ and Eu$^{2+}$. In lanthanide series, the progressive filling of electron in the shielded inner 4f orbital leads to gradual decrease in the ionic radii from La$^{3+}$ to Lu$^{3+}$, which is called lanthanide contraction. With decreasing ionic radii, there is a systematic change in the strength of complexation between REEs and ligands (de Baar et al., 1991; Hemberger et al., 2004). Due to this difference, they are used as tracers in studying fundamental processes that govern the oceanic cycling of REEs. For instance, the heavier lanthanides were predicted to be more strongly complexed in seawater and hence more resistant to scavenging (Michael, 1999). The fractionation between particles and ligands in solution depends on the relative affinities of these phases in the REEs (Turner et al., 1981; Sholkovitz, 1993; Kelly et al., 2004). The most important source of REEs is riverine input. The concentrations of REEs in river waters are significantly higher than seawater (Elderfield et al., 1988). The behaviors of REEs in rivers and estuaries have been used to understand the geochemical exchange between the crust and the ocean (Elderfield et al., 1988). The large-scale removal of light REEs occurs during estuarine mixing. Planktonic uptake, coprecipitation with non hydroxides, and salt-induced coagulation of colloids has been suggested as their removal mechanism (Martin et al., 1976; Feely et al., 1981; Hoyle et al., 1984; Sholkovitz, 1992).
These processes in a way, reduces the effective flux of REEs into the ocean (Martin et al., 1976). The major process that removes metals from water is adsorptive scavenging by sinking particles, which controls the distribution of many reactive elements in the ocean (Dorte and Yoshiyuki, 1998).

The elements Ce and Eu exhibit different oxidation states. Although Ce is well accommodated in the igneous rocks, oxidation of Ce$^{3+}$ to Ce$^{4+}$ proceeds in oxygenated systems. The Ce$^{4+}$ hydrolyzes readily in seawater, but tends to be removed by scavenging. For this reason, Ce is often enriched in some authigenic minerals such as manganese nodules and phosphorites, while it remains depleted in seawater. Eu will be reduced to Eu$^{2+}$ by magmatic processes, which is larger than other REEs (Sun and McDonough, 1989). Anomalous concentrations of Eu are not uncommon in igneous and sedimentary rocks. Eu enrichment has been observed in hydrothermal vents at mid-oceanic ridges (Debra and Peter, 1999). The Ce anomaly due to oxidation–reduction reactions can be evaluated relative to the trivalent neighbors (La and Pr) in the lanthanides series without significant influence of the other processes affecting their oceanic distributions (Graham and Peter, 2001). In natural waters, the REEs exist in the trivalent state apart from Ce, which is the only REEs with redox transformations (Goldberg et al., 1963; Elderfield, 1988; Pernilla et al., 2008). However, the Ce (III) has a chemistry similar to its trivalent neighbors (La and Nd) and hence, its oxidation to Ce (IV) results in the formation of a less soluble form. The extent to which Ce is fractionated can be quantified by the Ce anomaly, which is a measure of the observed Ce abundance to that expected for trivalent Ce. A value of 1 means that all three REEs have a crust-like composition and that Ce is not fractionated from its trivalent neighbors. By definition, values between 0 and 1 are called negative anomalies while values above 1 are called positive anomalies. Large negative anomalies (0.1-0.5),
typical of saturated water indicate the preferential removal of the less soluble Ce$^{4+}$ (Elderfield, 1988; Piepgras and Jacobsen, 1992; Dubinin, 2006; Yoshitaka, 2008). This is an advantage of this element over other transition metals, which are individually affected by the oxidation states. The composition of rocks and minerals is extensively used as an indicator of evolution of the Earth (Taylor and McLennan, 1985; Arifudin et al., 2007). The geochemical reactions fractionate REEs at low temperatures in sediment and water (Goldstein and Jacobsen, 1987; Braun et al., 1990; Johan et al., 2000).

Uranium and thorium coming under actinide series are found commonly in environment. In nature, uranium exists as $^{238}$U (99.284 %), $^{235}$U (0.711 %) and $^{234}$U (0.0058%). Uranium decays slowly by emitting an alpha particle. The half-life of uranium-238 is about 4.47 billion years and that of uranium-235 is 704 million years, which make them useful in estimating the age of the Earth (uranium-thorium dating, uranium-lead dating and uranium-uranium dating). Uranium in the ocean is an element which has a long oceanic residence time of more than one million years (Goldberg et al., 1971), probably due to the fact that $^{4+}$U forms a stable complex $\text{UO}_2\text{CO}_3^{4+}$ in oxic seawater (Garrels and Christ, 1965). On the other hand, $^{4+}$U under anoxic condition is unstable and probably exists in the form of hydroxides or oxide (uranite). This suggests that U has no definite sink in oxidizing environment, whereas coastal sediments act as a trap of U (Heye, 1969). Thorium is a natural radioactive metal and is about three times more abundant than U in rocks and soils. Thorium occurs in several minerals, the most common source being thorium phosphate mineral monazite. $^{232}$Th decays very slowly (its half-life is about three times the age of the earth), but other thorium isotopes occur in uranium's decay chains.
1.3 Previous studies

The continental shelf and coastal region are the most sensitive zone of any country and it is essential to initiate constant monitoring of the region. Metal pollution is one of the major threats to coastal zone worldly. Several studies are reported on the distribution, bioavailability and accumulation of metals in highly contaminated shelf areas and estuaries of temperate regions (Nolting, 1986; Bryan and Langston, 1992; Everaarts and Fischer, 1992), subtropical and tropical regions such as the Mediterranean Sea (Voutsinou-Taliadouri and Satsmadjis, 1983; Catsiki et al., 1991; den Das and Nolting, 1993), Java Sea and adjacent coastal zone (Everaarts, 1989), estuarine and coastal areas of the Gulf of Thailand (Windom et al., 1984; Hungspreugs et al., 1989; Everaarts et al., 1994; Censi et al., 2007), estuarine and coastal regions of China (Zhang and Wang, 2001; Zhang et al., 2002) etc. Studies on the sedimentary environment have established that most of the shale sediments are uniformly enriched in the light rare earth elements (LREEs) relative to the heavy rare earth elements (HREEs), when normalized to chondrite (Haskin and Gehl, 1962; Fleet, 1984). Haskin et al. (1966) and Sholkovitz (1990) reported that shale- normalized terrigenous inputs from land do not display significant Ce anomalies. McLennan (1989) studied about the influence of provenance and sedimentary processes on REEs in the sedimentary rocks. Murray et al. (1991) studied REEs in Japan Sea sediments along with Ce anomalies. Nath et al. (1992) studied REEs patterns of Central Indian basin sediment related to their lithology. Pattan et al. (1995) studied the distribution of major, trace and rare earth elements in surface sediments of the Wharton basin and observed that REEs in this sediment reflect a combination of surface water properties and diagenetic processes. Ross et al. (1995) studied the positive Eu anomalies along Manso
River by REEs normalisation. The REEs enrichment is associated with high pH, while the feldspars and their secondary products are the cause of Eu anomaly. There are environmental studies of similar nature from other regions as well (Araujo et al., 2002; Borrego et al., 2004; Michael and Kamber, 2006; Carman et al., 2007; Marmolejo et al., 2007; Kurian et al., 2008; Ergul et al., 2008).

The chemical oceanographic features of Arabian Sea have been exhaustively studied by Banse (1959), Reddy and Sankaranarayanan (1968), Sen Gupta et al. (1980), Naqvi et al. (1993; 2000), Naqvi and Jayakumar, (2000), Jyothibabu et al. (2008), Thresiamma et al. (2008), and Balachandran et al. (2008 a and 2008 b). The studies by Hashmi et al. (1981) revealed deposition of clay-sized sediments in the nearshore regions by the process of flocculation, which resulted in trapping of coarse particles in the Cochin-Kollam coast. Compared to cross shelf transport, along shelf transport appears to be the more dominant mechanism for sediment transport on the western continental shelf of India (Ramaswamy, 1987). Ramaswamy and Nair (1989) have reported that the anthropogenically-derived pollutants, associated with clay particles discharged from the coast, would tend to remain within the narrow confines of the inner continental shelf. The shoreline along Cochin has been classified under barrier beaches and the changes in morphology in response to different seasons are studied by Prasannakumar and Murthy (1987). Studies on the heavy-mineral suit of the coastal and river sediments of Kerala have the terrain constituted by opaques, horn-blende, hypersthene, tremolite/actinolite, pyroxene, epidote, zieron, silimite, Kyanite, staurolite, and alusite, monazite, rutile, spene, apatite and tourmaline (Reddy and Rao, 1992). They have observed differential wave activity together with static mud suspension at places in the nearshore region.
Recently, there are studies reporting the metal geochemistry in water and sediment in Arabian Sea (Prakash babu and Nath, 2005; Balakrishnan et al., 2005; Laluraj and Nair, 2006; Rejomon et al., 2008). Nath et al. (1997) studied the trace and rare earth elemental variation in Arabian Sea across the oxygen minimum zone (OMZ). They analyzed sediment samples beneath the intense OMZ and away from the OMZ and found that Ce anomaly showed not much significant differences between these two regions. However, earlier reports on geochemistry of sediments along the central southwest coast of India are limited to Murthy et al. (1973), Rao et al. (1974), Rajamani (1994), Nath et al. (2000), Balachandran et al. (2005) and Laluraj and Nair (2006) with only very few samples to represent the environment. The work of Nath et al. (2000) furnishes an insight to the provenance of rare-earth elements in the fluvial fraction (< 4 mm) that also date back to one set of sampling during 1981. Inadequacies in all the above studies have been their proper addressing of the influence of oceanographic and sedimentary processes to the metal geochemistry. Such studies require increased density of sampling covering seasonal signals, which play an important role when coastal regions are considered.

A number of multidisciplinary studies have been undertaken in the Cochin estuary during past several decades. The reduction in the carrying capacity of the backwaters, disruption in the life cycle of organisms, destruction of natural habitats, accumulation of pollutants, salt water intrusion, symptoms of eutrophication, over exploitation and dwindling of resources etc. stress the need for the conservation of the ecosystem. Some of the important works worth mentioning in this context (Ramamirtham and Jayaraman, 1963; Murthy and Veerayya, 1972; Venugopal et al., 1980; Nair et al., 1990; Nair et al., 1994; Thresiamma et al., 1998; Sheeba, 2000;
Srinivas, 2000; Unnikrishnan and Nair, 2004; Balachandran et al., 2005; Laluraj et al., 2005; Geetha et al., 2006; Srinivas and Dinesh Kumar, 2006; Babu et al., 2006; Kalesh and Nair, 2006; Laluraj and Girish, 2006; Laluraj et al., 2006a). Partitioning of marine and estuarine sediments of this region has been carried out by Shibu et al. (1990); Nair, (1992), Rajamani, (1994), Shibu et al. (1995). The levels of trace metals in the water and particulate matter of Cochin estuary are reported by Nair et al. (1990, 1991), Suraj et al., (1996), Balachandran et al. (2005). Balachandran et al. (2006) has studied clay mineralogy of Periyar river sediments and their role in the uptake of metals. Nath et al. (2000) studied the provenance, weathering and distribution of rare earths, major and trace elements of the fine grained fraction of the bed load sediments from Cochin estuary and adjoining coastal region. They found salt induced adsorption/desorption mechanism for trace and rare-earth elements in Cochin estuary.

Being one of the largest sources of freshwater and continentally derived metals to the southeastern Arabian Sea, the Cochin estuary exhibits a range of hydrographical and geochemical properties, which modify the biogeochemical cycles of metals. The recent studies on the physical, sedimentological, biological, and chemical parameters have been discussed in detail about the different processes operating in the Cochin estuary (Laluraj et al., 2007; Narayana et al., 2007; Priju and Narayana, 2007; Renjith and Chandramohanakumar, 2007; Laluraj et al., 2008; Martin et al., 2008; Balachandran et al., 2008c; Padmalal et al., 2008).

1.4 Aim and scope of the present study

The basic requirement to characterise an environment is to synthesize systematic data at close grids of the region covering different seasons and to compare the results with existing processes in the region. An integrated study
of this dimension has not been carried out so far along the southwest coast of India, which has been taken as the basic objective of this study. Eventhough information is available along the continental shelf of India, these data are collected from limited locations without considering the seasonal variability or frequency of more than one degree and well beyond in areas with depths > 30 meters. Considering the global demands of REEs as a mineral resource and its high abundance along the southwest coast of India, this region especially demands a comprehensive and systematic exploration to unravel the geochemical distribution of various elements. Similarly, the geochemical characteristics of the largest estuarine complex in the study region (Cochin estuary) will also compliment the above endeavor. With a view to delineate environmental changes and to evaluate the sediment geochemistry of the region, a detailed study on the non-transition, transition and rare-earth elements including uranium and thorium, and the parameters which affecting their adsorption/desorption mechanism have been undertaken along the continental shelf of Kerala and the Cochin estuarine system.

One of the greatest coincidence of the present study was that the two exhaustive sample collections were interspaced by a Catastrophe. It was during this period (December 2004) that the southern tip of Indonesia experienced a submarine earthquake (Mw 9.3) causing a tsunami, which was among the deadliest disasters in modern history (Laluraj et al., 2006b). This tsunami devastated the shores of Indonesia and several southeast Asian countries including India. Massive damage to the livings and non-living was inflicted along the coastal regions of Tamil Nadu, Andhra Pradesh and Orissa (east coast of India) and, Karnataka and Kerala (west coast of India) following the waves generated by the tsunami (Reddy et al., 2005). Cochin Estuary also experienced the ferocity of this tsunami (Laluraj et al., 2007). It
has been estimated that the tsunami has caused high velocity waves (~ 700 km/hr) along the west coast of India, causing an elevation of about 2 m at Goa. Although there has been a different interpretation on the impact of tsunami on the oceanic realm, there were severe limitations in comparing the post tsunami scenario features with its previous conditions. The present study therefore, form an unambiguous analysis of the mineralogy and geochemistry of sediments along the southwest coast of India during the two periods of prior (July 2004) and after (March 2005) tsunami. A similar attempt was also possible to assess the impacts of tsunami on Cochin estuary. Hence, this study has gained invaluable significance as it can provide one of the realistic views on the impact that the tsunami has caused on the sedimentary environment along the southwest coast of India.

1.4.1 Objectives of the study

1. Study the seasonal variability of physio-chemical and sedimental characteristics along the shelf of Kerala and Cochin estuarine system.

2. Study the influence of seasonality and sediment texture on the geochemical distribution of elements along the shelf of Kerala and Cochin estuarine system.

3. Decipher the seasonal distribution of non-transition elements in sediments along the two environments.

4. Evaluate the geochemical index of transition elements in the two sub environments.

5. Study the seasonal variability of the rare earth elements along the coastal belt of Kerala in comparison to Cochin estuarine system.

6. Estimate the seasonal variations in the enrichment and excess of non-transition, transition and rare earth elements in sediments along the two environmental sections.
7. Estimation of the levels of metals such as Ga, Pr, Dy, Ho, Er and Tm in the Cochin estuary.

8. Study on the sedimentary geochemical interactions using statistical tool such as linear and multiple regressions.

9. Model representation on the geochemical distribution of transition metals along the shelf and estuary during different seasons.

10. Evaluate the impact of tsunami on the texture and composition of the sediments along the shelf of Kerala and Cochin Estuary.

11. Illustration of possible mechanisms on the accumulation of metals in sediments of the two environments.

12. Comparison of elemental enrichment in sediments along the shelf and Cochin Estuary.

1.5 References


Banse, K. 1959. On upwelling and bottom-trawling off the southwest coast of India. Journal of Marine Biological Association of India. 1, 33-49,


Dubinin, A.V. 2006. Cerium anomaly as the indicator of phase transformations of Fe-Mn authigenous minerals in the ocean. Geochimica et Cosmochimica Acta. 70, 149 -149.


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Marcus, W.A. 1996, Segment-scale patterns and hydraulics of trace metal concentrations in fine grained sediments of a cobble and boulder bed mountain stream, Southeast Alaska. Mountain Research and Development. 16, 211-220.


